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METHOD AND APPARATUS FOR PRODUCING CHLORINE DIOXIDE
IN WATER

(17)

Callera, Joseph, Rochester, New York, U. S. A.

Granted to Chemical Generators Inc., Rochester, New York,
U. S. A.

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FIELD OF INVENTION

The invention relates to the production of chlorine dioxide in water by the reaction of a metal chlorite with an acid.

5 BACKGROUND INFORMATION AND PRIOR ART

Chlorine dioxide is of considerable industrial importance and has found use in the bleaching of wood pulp, fats, oils and flour. Generally, chlorine dioxide is used as a bleaching agent and for removing undesirable tastes and odors from water, foodstuffs, and the like. More recently it has been used as an anti-pollutant. The use of chlorine dioxide is particularly popular in swimming pools. For several of the established uses of the chlorine dioxide, it is desirable to produce the gas in situ so that the chlorine dioxide, upon formation, can be directly put to use either in gaseous form or, after absorption, in the form of an aqueous solution. In many instances the use of chlorine dioxide in solution rather than in gaseous form is preferred. The production of chlorine dioxide in situ is particularly desired in order to avoid storage and shipping problems. In this connection it should be appreciated that prior art production of chlorine dioxide is hazardous and the substance per se is difficult to handle.

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It has previously been proposed to produce chlorine dioxide by subjecting an aqueous lithium chlorite solution to electrolysis in a cell, wherein the anode is separated from the cathode by a semi-permeable membrane. This proposal is thus based on electrical migration through a semi-permeable membrane resulting in dissociation of the lithium chlorite molecule.

According to more recent proposals alkali metal chlorites as well as alkaline earth metal chlorites are converted into chlorine dioxide by ion exchange.

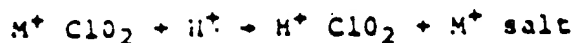
SUMMARY OF THE INVENTION

It is a principal object of the present invention to produce chlorine dioxide in water by direct reaction between a chlorite and an acid in which the reactants are supplied in such a form that the chlorine dioxide production can be readily effected in situ and without requiring any skill on the part of the operator or user.

Another object of the invention is to provide suitable equipment for the indicated purpose.

Briefly, and in accordance with the invention, aqueous chlorine dioxide is produced by introducing water into a receptacle which contains a chlorite of an alkali metal or an alkaline earth metal and an acid. The chlorite and the acid are each separately wrapped or packed in a water soluble envelope or container so that upon the introduction of water into the receptacle, the water soluble envelopes dissolve, thus permitting the reactants, to wit the chlorite and the acid, to react and to form chlorine dioxide which is immediately absorbed by the water to form an aqueous chlorine dioxide or chlorous acid solution.

The reaction is essentially predicated on the following equation:



wherein M stands for any alkali metal or alkaline earth metal while the hydrogen atom on the left side of the equation indicates the hydrogen of an acid.

As stated, any alkali metal or alkaline earth metal chlorite may be used for the inventive purposes. From a practical point of view, and also for economy reasons, the sodium chlorite and lithium chlorite are preferred.

Some of the alkaline earth metal chlorites have a tendency to form relatively insoluble salts with the acid, as for example calcium chlorite, and are therefore less desirable.

5 Concerning the acid it is preferred to use relatively weak acids since otherwise the reaction between the chlorite and the acid may be too violent and thus difficult to control. The choice of the particular acid will of course be dependent on the use to which the chlorine dioxide solution is to be put. Thus, for example, if the
10 chlorine dioxide is to be used for food processing purposes, an acid should be used which forms a salt with the metal moiety of the chlorite which is acceptable for foodstuff. Thus, for example, for such purposes citric acid and tartaric acid are particularly suitable, since their salts are
15 acceptable in foodstuffs in minor amount. However, it will be appreciated that the choice of the acid is not critical considered from the chlorine dioxide production point of view. Thus, for example, boric acid, carbolic acid, casamino acid, chloroacetic acid or chloroanilic acid or sulfanilic
20 acid may be used if the chlorine dioxide is to be employed for purposes such as, for example, the bleaching of wood pulp, wherein the presence of the corresponding salts would be innocuous. Acidic phosphate, phosphorous pentoxide, and other acidic substances, including strong acids such as
25 sulfuric acid or hydrochloric acid, could thus theoretically be used.

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However, tests have indicated that organic hydroxy acids and carboxylic acids give the best results since then a desirable non-exothermic reaction sets in. The reaction is essentially non-exothermic with monocarboxylic acid. With dicarboxylic acids some heat ^{evolution} ~~evolution~~ is observed. In this context it will be noted that known reactions of this kind are exothermic. In addition to citric acid and tartaric acid as previously mentioned, the following acids have proved to be particularly suitable: lactic acid, malic acid and glycolic acid. Oxalic acid and malonic acid result in an exothermic reaction while benzoic acid yields a weak and prolonged reaction only.

From a practical point of view it is preferred to supply the reactants in solid form and for this purpose predetermined amounts can be compressed into tablets or pellets which are then enveloped by a suitable material which, while initially sealing the reactants from the ambient atmosphere, readily dissolves upon contact with water. Polyvinyl alcohol film and certain cellulose films, which are readily available on the market, are particularly suitable for this purpose. The reactants are thus prepackaged within such water soluble film envelopes which advantageously are heat sealed. Instead of providing two separate envelopes, one containing the chlorite reactant and the other one the acidic reactant, a single pouch or envelope unit can be provided which contains two compartments, one containing the chlorite and the other one the acid, the two compartments being separated from each other by sealing seams or the like.

Although it has been stated that the reactants should advantageously be supplied in solid form, it will be appreciated that it is also feasible to envelop solutions of the reactants. In such event the enveloping material must, of course, not be water soluble.

The receptacle into which the reactant containing envelopes are placed prior to use should, of course, be of a material inert to chlorine dioxide. Experience has demonstrated that polyethylene bags are eminently suitable for this purpose.

The various features of novelty which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this specification. For a better understanding of the invention, its operating advantages and specific objects attained by its uses, reference should be had to the accompanying drawing and descriptive matter in which there is illustrated a preferred embodiment of the invention.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing :

Fig. 1 is a front elevational view of a disposable chlorine dioxide producing unit or kit in accordance with the invention, and

Fig. 2 is a view of a second embodiment.

Referring now to the drawing reference numeral 10 generally indicates a receptacle in the form of a polyethylene bag. The bag has an opening 1 which may be closed in conventional manner and is provided with a venting exit 2.

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 A discharge ^{or} of withdrawal tube 3 is connected to the bottom
 portion of the bag 10, the flow through the tube 3 being
 controlled by a valve 3a which may be in the form of an
 ordinary clamp or the like. The bag is also provided with
 5 suitable markings. Thus, the Figure indicates a first marking 4
 which may be labelled "reaction level" and a second marking 5
 which may be labelled "one gallon dilution level".

10 When chlorine dioxide is to be produced the bag
 is suitably suspended from a support such as a wall or a post
 (not shown) and for this purpose a suspension hook or strap,
 generally indicated by reference 6, is provided. The reactants
 are then inserted into the opening 1. In the embodiment here
 shown the reactants are solid sodium chlorite and citric acid
 also in solid form. The two reactants are each accommodated
 15 in compartments 7 and 8 of a pouch, generally indicated by
 reference 20, which is made from a water soluble film material
 such as polyvinyl alcohol. The two compartments 7 and 8 are
 heat-sealed from each other, the heat-sealed seam being
 indicated by reference 9. The ~~reactants sodium chlorite~~
 20 ~~and citric acid are thus protected from each other and the~~
 ambient atmosphere. Water is now poured through the opening 1
 up to the reaction level marking 4. The water dissolves the
 polyvinyl alcohol film and the reaction between the sodium
 chlorite and the citric acid takes place. In order to accelerate
 25 the reaction, the bag 10 may be slightly squeezed or
 shaken to cause some agitation of the water. Once the reaction

between the chlorite and the acid has taken place, which in practice occurs within a very brief period of time, more water is poured through the opening 1 and up to the one gallon dilution level 5. After the water has been added the opening is closed in order to prevent escape of chlorine dioxide gas. However, the vent opening 2 should preferably remain open so as to avoid any excess pressure. The chlorine dioxide solution thus formed may be directly supplied to the place of use by opening the valve 3, whereupon the solution will flow through the tube 3. In the event that it should be desired to obtain and use the chlorine dioxide in pure form, to wit, without the presence of the metal salt which has been formed, to wit, in the present instant sodium citrate, a pipe (not shown) may be inserted into the bag and air or the like inert gas may be blown through the pipe, whereupon gaseous chlorine dioxide will escape through the venthole and thus may either be supplied directly to the place of use or may be absorbed in pure water to form a pure chlorine dioxide water solution.

It will be appreciated that instead of providing a single envelope unit 20, having two compartments 7 and 8, two separate envelopes, one containing the chlorite and the other one the acid, may be used instead.

As has been indicated, it is preferred if the water is added in two stages, to wit, a first stage in which the bag is filled up to the reaction level marking, and a second stage in which the bag is filled up to the dilution marking. Of course, it is feasible to add the water in one step but this will retard the reaction and from a practical point of view it is preferred if stagewise addition of the water is accomplished.

According to the second embodiment of Fig. 2 a kit is shown which is particularly suitable for producing chlorine dioxide in situ in a relatively large body of an aqueous liquid, such as for example, a swimming pool. The kit comprises a bag 20, shown in front elevation which has a number of openings or perforations 21. Water soluble envelopes 22 and 23 are accommodated within the bag 20, the envelopes respectively containing chemicals I and II of which chemical I is the chlorite while chemical II is the acid. When the bag is thrown into the swimming pool, water will enter the space defined by the bag and will dissolve the water soluble envelopes 22 and 23. This in turn results in the reaction between chemicals I and II whereby chlorine dioxide is formed. The reaction, however, is substantially confined to the space defined by the bag 20. After the reaction has been

completed the bag may be squeezed and removed so that its contents flow into the swimming pool. However, it is also feasible to make the bag 20 of a water soluble material somewhat thicker than the material of the water soluble envelopes 22 and 23. In such event the bag or receptacle 20 will thus also dissolve after some time but only after the envelopes 22 and 23 have dissolved. In this manner removal of the bag 20 from the swimming pool or the like body of liquid would be rendered unnecessary. The above embodiment constitutes a very practical kit in which the reaction area is effectively restricted. The above embodiment is, of course, also very suitable for use in water towers, water circulating systems and the like.

The invention will now be described by several examples, it being understood that these examples are given by way of illustration and not by way of limitation and that many changes may be effected without affecting in any way the scope and spirit of the appended claims.

Example 1

13.5 g of sodium chlorite Na ClO_2 in powder form were prepacked in a polyvinyl alcohol envelope and the envelope was heat-sealed. A second heat-sealed polyvinyl alcohol film envelope containing 29 g of citric acid was prepared. The two envelopes were dissolved in one liter of triple distilled water. 9.7 g of chlorine dioxide ClO_2 were formed, the amount of chlorine dioxide being determined spectrophotometrically by comparison with a standard curve. Positive identification of citrate ion was made. It was established that essentially pure chlorine dioxide and sodium citrate had been formed.

Example 2

5 The test of Example 1 was repeated but the chlorite reactant was 13.5 g of sodium chlorite while the acid was 14 g of tartaric acid. 9.7 g of chlorine dioxide were formed.

Example 3

The test of Example 1 was repeated the reactants being 13.5 g of sodium chlorite and 9.8 g of benzoic acid. 9.7 g of chlorine dioxide were found.

Example 4

10 Examples 1, 2 and 3 were repeated, but instead of supplying the reactants in powder-form they were compressed into tablets or pellets in a tablet press. The same results were obtained.

Example 5

15 Examples 1, 2 and 3 were repeated, but the polyvinyl alcohol film material was replaced by commercially available water soluble cellulose film materials. The same results were obtained.

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In all the examples heretofore described the sodium chlorite was used in milled or ground condition so as to reduce the particle size. However, technically available coarse material can also be used. This, however, affects the reaction time since the reaction between the sodium chlorite and the acid proceeds slower if the chlorite has a larger particle size. If slow reaction is desirable the particle size should therefore be increased.

Example 6

Examples 1, 2 and 3 were repeated, but the respective reactants were supplied in the form of concentrated aqueous solutions, the water soluble polyvinyl alcohol or cellulose film being replaced by water resistant plastic foils. In order to initiate the reaction the foils were torn open. The results were the same.

While the reaction between chlorite and strong acid is rather violent and thus may conceivably result in the production of an undesirable byproduct such as chlorine, the inventive reaction between the chlorite and relatively weak acids is predictable and does not normally result in formation of byproducts. A steady flow of chlorine dioxide is produced and by suitably premeasuring the reactants excellent yield of chlorine dioxide is obtained.

For food processing purposes, the use of citric acid and tartaric acid is preferred because these acids are generally acceptable in the food industry as far as compatibility with food is concerned and also to the extent that these acids and their salts do not in themselves act as pollutants in aqueous systems. Another important consideration in this respect is the degree of acidity which these acids discharge. They are safe and easy to handle, do not promote corrosion to a significant degree and, of course, are edible.

Example 7

This Example deals with the dilution, concentration and stability of the chlorine dioxide solution. The tests were carried out with sodium chlorite and citric acid as the reactants. The reactants were supplied in amounts so as to obtain a 30% aqueous chlorine dioxide solution. The optical density was determined at various time intervals and the concentration of chlorine dioxide was calculated from the optical density. The following result was obtained:

Solution	OD Sample	Storage Time	Approximate Concentration of ClO_2 calculated from OD Curve
30%	1.921	0	30
	1.506	5 min.	25
	1.203	10 min.	20
	1.000	25 min.	15
	.861	2 hr.	8
	.840	6 hr.	8
	.840	12 hr.	8
	.840	24 hr.	8
	.840	48 hr.	8
	.725	1 wk.	7
	.691	3 wk.	4
	.320	6 wk.	3

It will be noted that while the solution originally contained 30% of chlorine dioxide, the optical density decreased already after five minutes of storage time to a concentration of 25%. An 8% concentration remained after two hours and this concentration was stable for about 48 hours. After 6 weeks of storage the concentration had dropped to 3%. It follows that solutions containing very high concentrations of chlorine dioxide do not remain stable and thus, are only useful if they are used substantially immediately or are substantially immediately diluted. Thus, for example,

if the chlorine dioxide is used for bleaching purposes high concentrations can be prepared, provided the solution is soon added to the bleaching bath.

Solutions containing initial concentrations of 20, 10 and 5% chlorine dioxide were then prepared according to the following table:

	Solution	OD Sample	Storage Time	Approximate Concentration of ClO_2 calculated from OD Curve
10	20%	1.200	0 min	20
		.999	20 min	15
		.858	2 hr	8
		.636	48 hr	3
		.705	1 wk	7
15	10%	.950	0	10
		.950	24 hr	10
		.950	48 hr	10
		.700	1 wk	7
20	5%	.530	0	5
		.580	48 hr	5
		.580	1 wk	5
		.560	2 wk	5
		.540	3 wk	5
		.536	4 wk	5
25		.515	5 wk	4.5
		.520	10 wk	4.5
		.515	12 wk	4.5

5 It will be noted that the best results are obtained with 5% solutions which remain stable for more than 4 weeks. After 12 weeks' storage the chlorine dioxide concentration is still 4.5%. The 10% solution remains stable for about 48 hours. It follows that from the practical point of view it is not advisable to prepare solutions containing more than 10% of chlorine dioxide if the solution is to be stored for any length of time. By contrast, 5% solutions have a long storage life.

10 Corresponding results were obtained when the citric acid was replaced by tartaric, aspartic or benzoic acid.

Example 8

Preparation of pure chlorine dioxide solution.

15 The system of Fig. 1 was connected with a second plastic bag filled with water. A tube was inserted in the plastic bag of Fig. 1 and a plastic tubing in the second bag was connected to the vent opening 2. Air was then forced through the plastic tube in the bag of Fig. 1 so that chlorine dioxide gas was liberated and escaped through the vent and the tube connected thereto to be discharged into the water
20 contained in the second bag.

Table of Recovery

1st bag % ClO_2 in Solution 2nd bag recovery of ClO_2 as percent

10%	4 min.aeration	9.3%
5%	4 min.aeration	4.5%
20%	8 min.aeration	17.5%
30%	15 min.aeration	25.3%

It will be noted that almost quantitative recovery of chlorine dioxide in the second bag is obtained.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A relatively stable aqueous solution of chlorine dioxide, said solution being free from toxic ingredients and containing the chlorine dioxide in free form and in a concentration of about 0.1 to 4.5% by weight, said chlorine dioxide being in ionic equilibrium with an organic acid salt.

2. A solution as claimed in claim 1, wherein said organic acid salt is an alkali metal or alkaline earth metal salt of citric acid or tartaric acid.

3. A solution as claimed in claim 1, wherein said organic acid salt is an alkali metal or alkaline earth metal salt which is acceptable in foodstuffs.

4. A method of producing aqueous chlorine dioxide by a substantially non-exothermic reaction, which comprises introducing water into a receptacle containing separate amounts of a chlorite of an alkali metal or an alkaline earth metal and an organic hydroxy acid or a carboxylic acid, said water, said chlorite and said acid being employed in amounts such that a stable chlorine dioxide solution of a concentration of not more than about 5% by weight of chlorine dioxide is obtained in which the chlorine dioxide is in ionic equilibrium with the simultaneously formed organic acid salt, said solution being free from toxic ingredients.

5. A method as claimed in claim 4, wherein the acid is citric acid or tartaric acid.

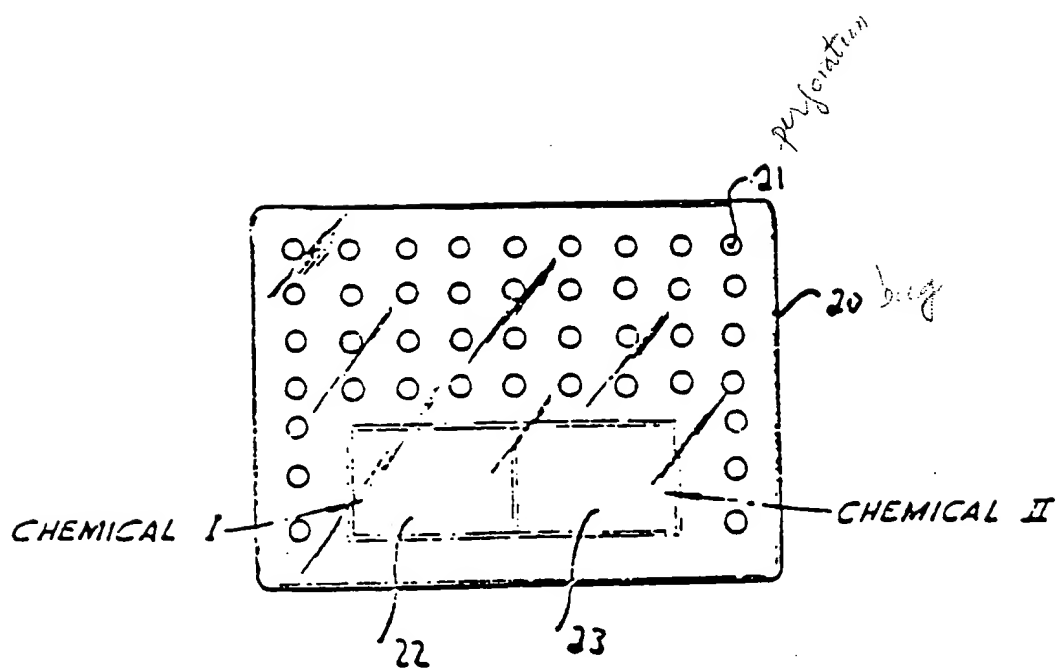


FIG. 2

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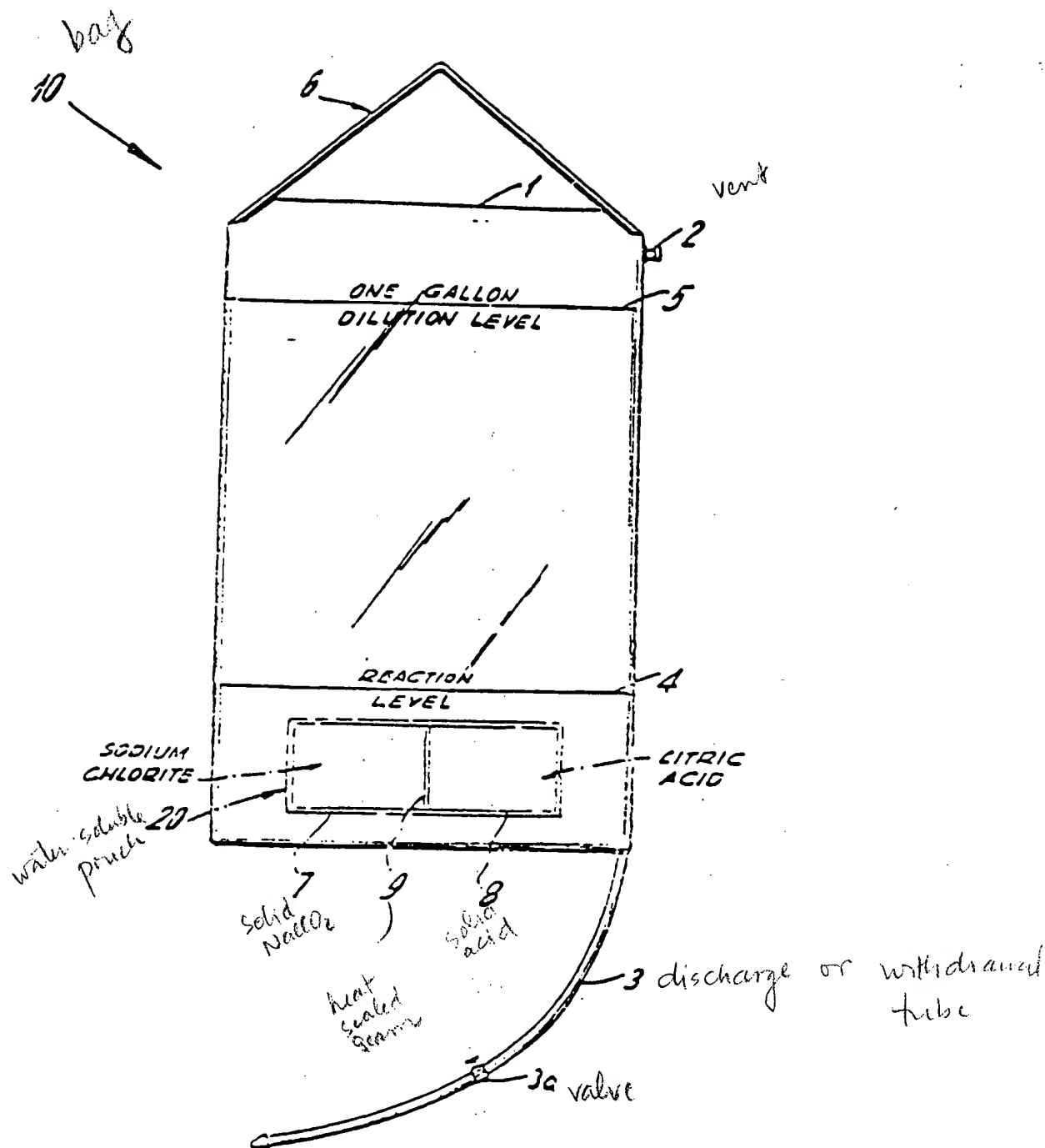


FIG. 1

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